

# **The Plusses and Minuses of Ethanol and Alkylates for Gasoline blending A Carmaker's Perspective**

***Lawrence Livermore National Laboratory Workshop on  
the Increased Use of Ethanol and Alkylates in  
Automotive Fuels in California***

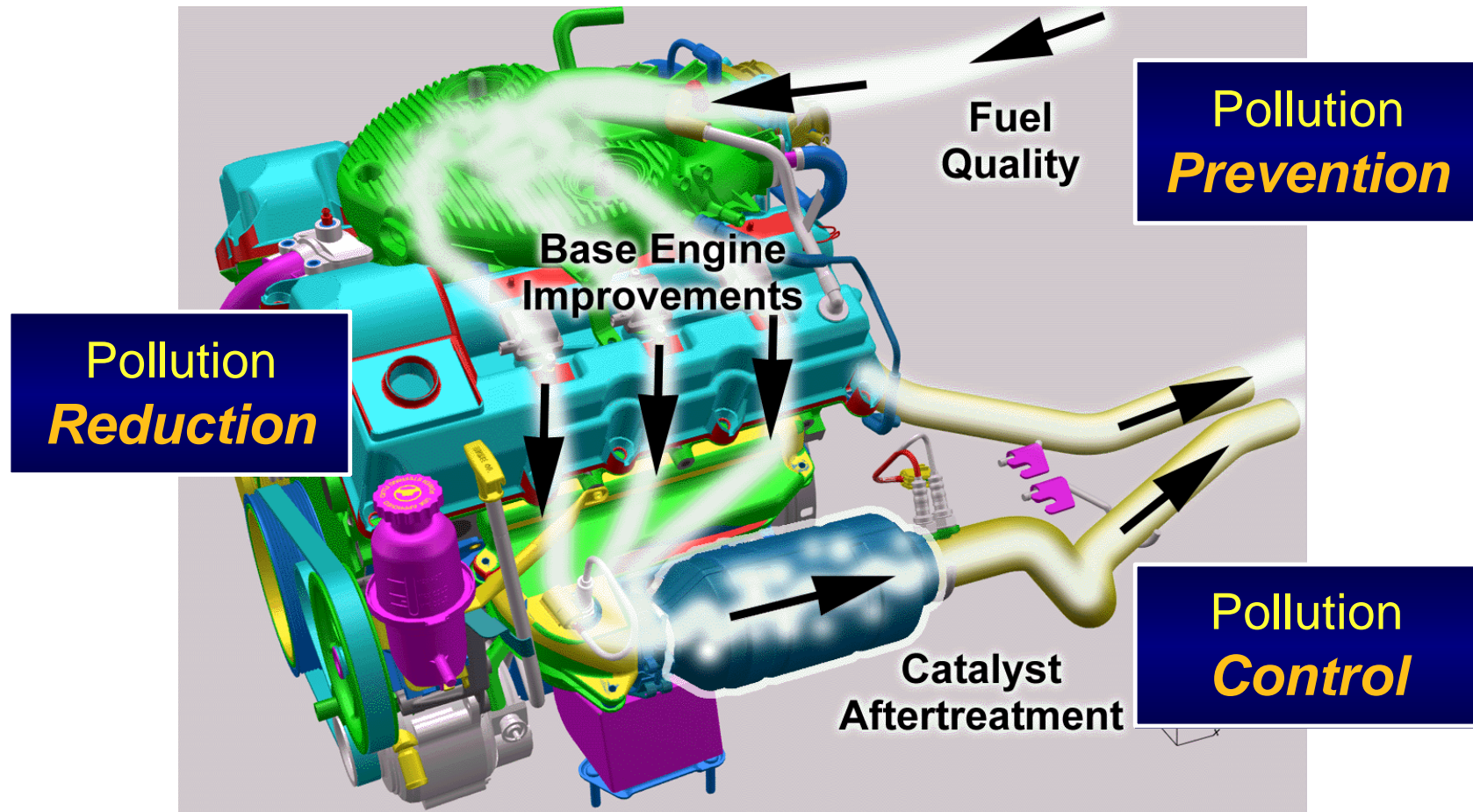
***April 10-11, 2001***

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## The Vehicle/Fuel as a System Approach

- Throughout the process of the development of low emission vehicles and reformulated gasoline, the ARB has treated the vehicle and its fuel as a system
- Considerations of neither vehicle emissions standards nor fuel properties should be undertaken without consideration of impacts on the other
- The MtBE/groundwater issue in California brings another component to the system -- the environment in which fuels are transported and stored

# Systems Approach - Pollution Prevention



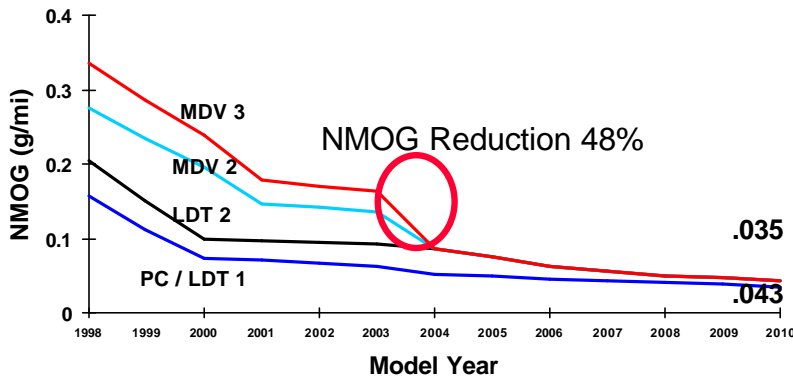
# **The Success of California CBG**

- LEV II Staff Report states, “ ... tenet of the original LEV program is that the vehicle technology and fuels must be linked to achieve the greatest emission reductions”, i.e., improvements in vehicle hardware should be accompanied by improvements in fuel quality
- “Cleaner-burning gasoline is the single biggest smog-reduction measure in California since the introduction of the catalytic converter in 1975 ... No single measure in our history has reduced pollution by such a large amount in such a short time. California gasoline now is the cleanest in the world.” -- ARB, October, 1996

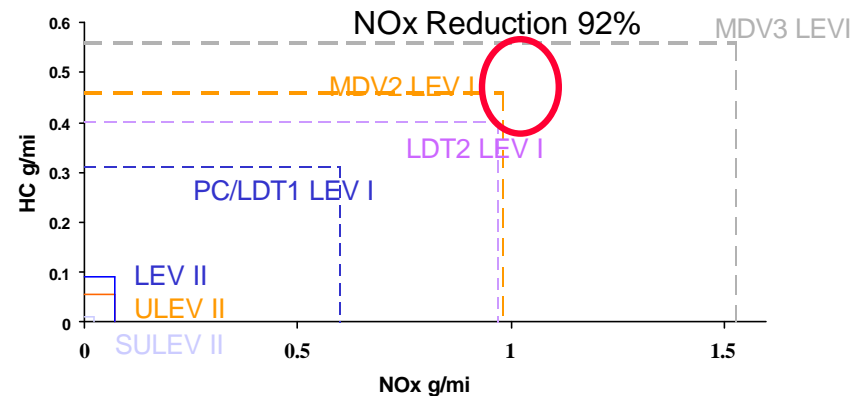
# **ARB Found Need for and Adopted LEV II Standards - ARB Staff Report November 15, 1998**

- **“State and federal air quality standards continue to be exceeded in regions throughout California”**
- **SIP called for adoption of technology-based emission control strategies for light-duty vehicles beginning in 2004 MY**
  - **Emission reductions of 25 tpd ROG+NOX by 2010 in South Coast**
  - **Additional technology measures, mobile source “Black Box”, needs of 75 tpd**
  - **LEV II “make(s) progress on the Black Box”**
- **“Emission reductions are needed statewide.”**
- **“The exhaust standards proposed in this rulemaking present a significant challenge to automobile manufacturers over the next ten years.”**

# ARB LEV-II Vehicle TP Emission Requirements



- The LEV II vehicle emission standards cut emissions from some vehicles by over 92%, and all tailpipe and evaporative standards are tightened



# Fuel / Vehicle System Synergies for Improved Air Quality

## GASOLINE PROPERTIES FOR LEV II

CALIFORNIA LEV II ISSUE	GASOLINE PROPERTY ENABLER
0.010 g/mi NMOG (SULEV)	Lower Sulfur Aromatics Control Volatility Control
0.05 g/mi NO <sub>x</sub> (LEV/ULEV)	Lower Sulfur, Lower Olefins Deposit Control Narrow band of oxygen content
0.01 g/mi PM <sub>10</sub>	Lower Sulfur Deposit Control Heavy Aromatics
120,000 Mile Durability (150,000 Mile Optional)	Lower Sulfur Deposit Control
Trucks to Car Standards	Lower Sulfur Deposit Control Volatility Control
OBD II Monitors	Lower Sulfur Volatility Control
SFTP	Lower Sulfur Volatility Control Narrow band of oxygen content
"Zero" Evap. and Refueling	Control of RVP, T <sub>10</sub> , T <sub>50</sub> No Waivers for RVP, T <sub>50</sub> , T <sub>10</sub> , or T <sub>(V/L)</sub> = 20 for EtOH
Exhaust Reactivity	Lower olefins Poly-substituted aromatics control

# Gasoline Volatility

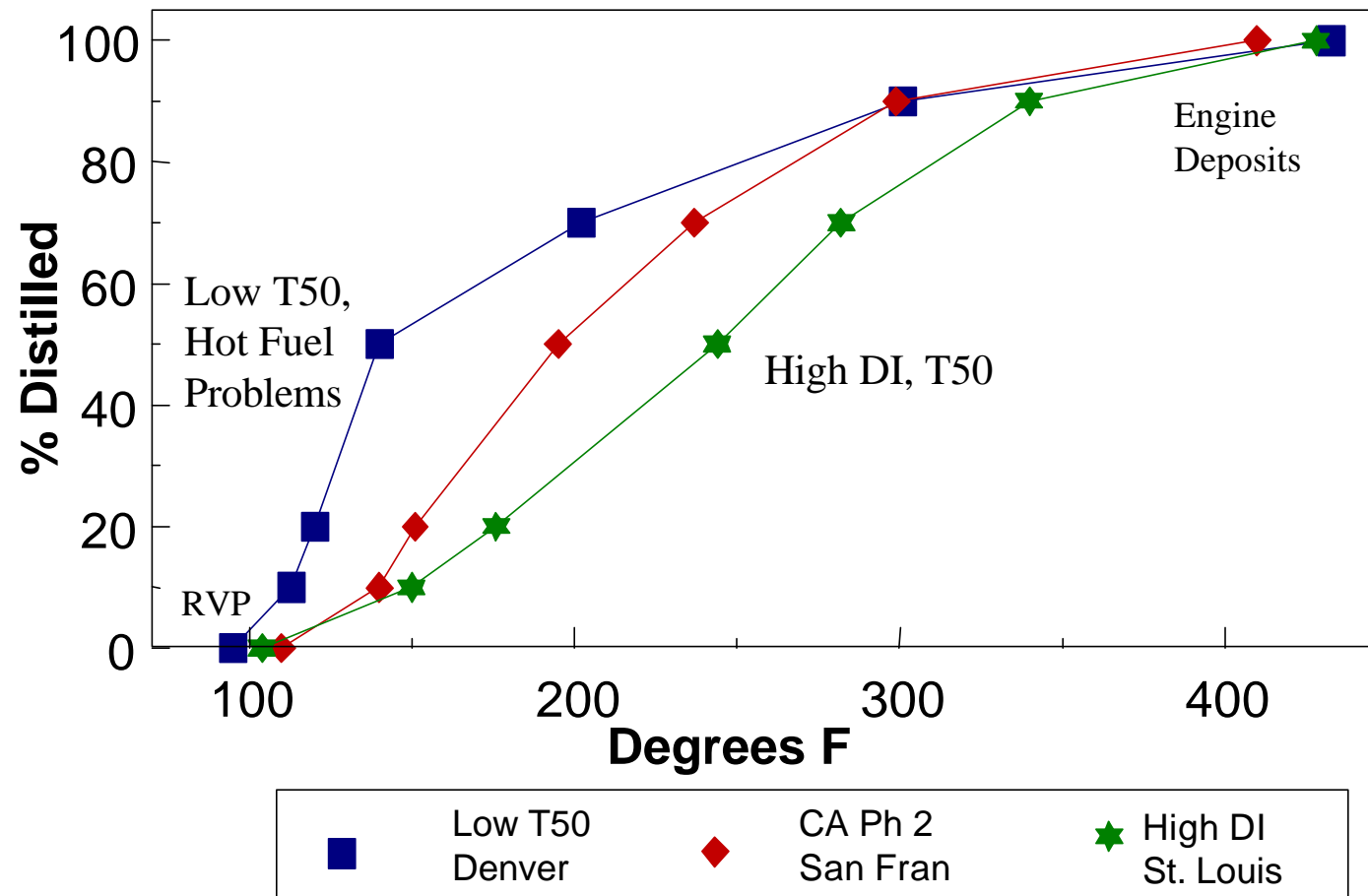
- Reid Vapor Pressure (RVP) of gasoline has been controlled as a means of reducing evaporative emissions
- However, other aspects of gasoline volatility, as measured by the distillation curve are important with respect to combustion. Unless constrained, these other volatility parameters (T-numbers) will increase as RVP is decreased
- Predictable gasoline volatility, as expressed in the distillation index (DI) is critical in maintaining a stoichiometric F/A ratio, which in turn is critical in reducing exhaust emissions. EPA recognizes that extremely tight control of F/A ratio is an enabler for tighter Tier 2 emissions standards



## Gasoline Volatility (cont.)

- **RVP is important to**
  - **Cold Weather starting**
  - **Hot weather vapor lock**
  - **Evaporative Emissions**
- **ASTM D86 Distillation**
  - **Defines entire gasoline boiling range**
    - **$T_{10}$ ,  $T_{50}$ ,  $T_{90}$  are the temperatures at which 10%, 50%, and 90% of a gasoline sample boils**
  - **The Distillation Index (DI) defines an empirical relationship between gasoline volatility and engine performance (driveability and emissions)**
- **$DI = 1.5 \times T_{10} + 3 \times T_{50} + T_{90} + 20$  (wt%oxy from EtOH)**

# Three Typical Gasoline Distillation Curves



San Francisco and St. Louis from AAMA Summer '97 Survey  
Denver from AAMA Fall '97 Shoulder Survey

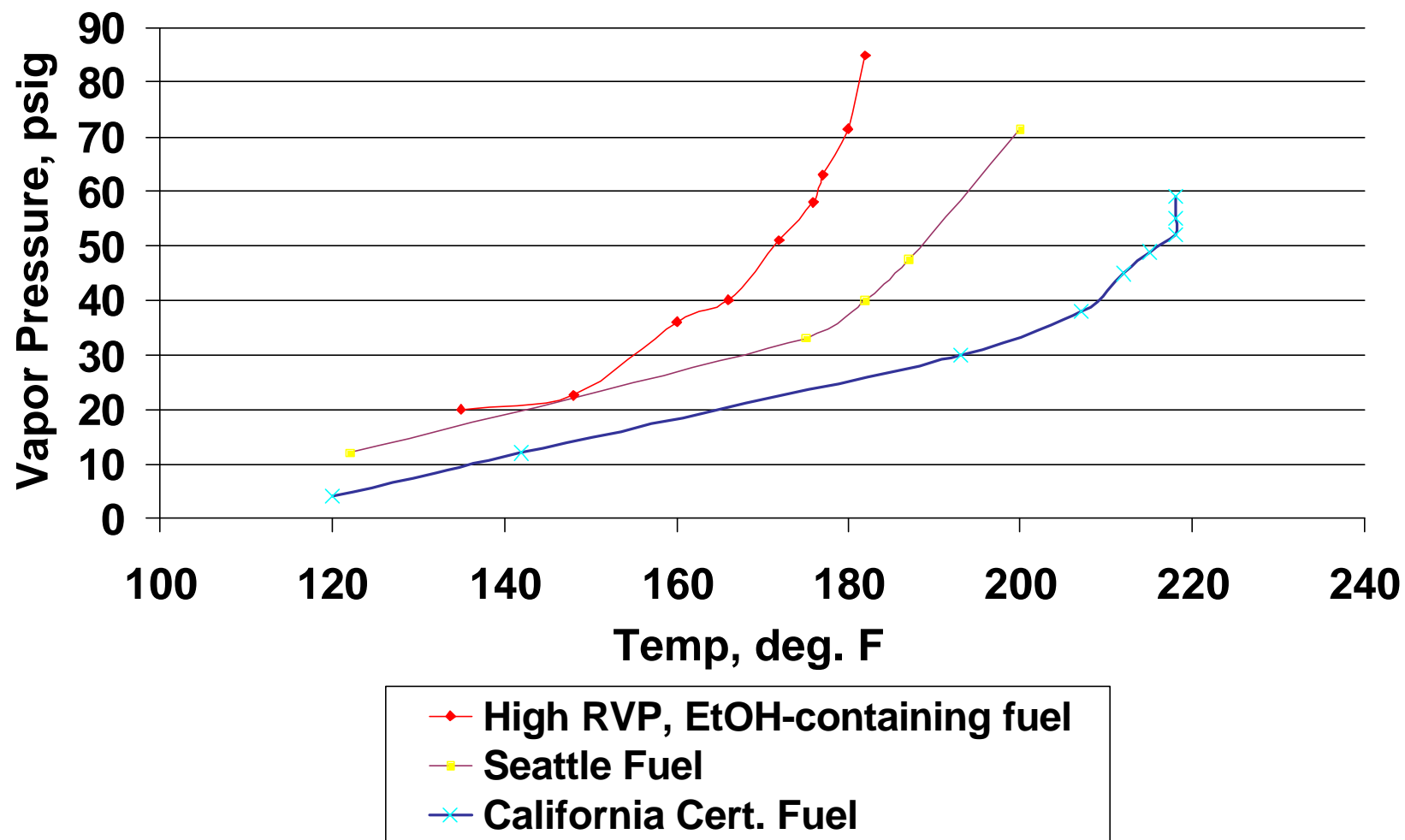
# The Impacts of Ethanol and alkylates on Gasoline Volatility

- C-8 alkylates boil higher than the current  $T_{50}$  of California gasoline, thus, their increased use will lead to higher  $T_{50}$ , and the associated problems
- Ethanol does not blend ideally with gasoline with respect to volatility. i. e. it does not follow the Clausius-Clapeyron behavior
- Ethanol raises RVP, and depresses  $T_{50}$ , but not the DI, which is related to engine performance
- The polarity of ethanol may lead to increased permeation of fuel compounds through plastics and elastomers in the fuel system

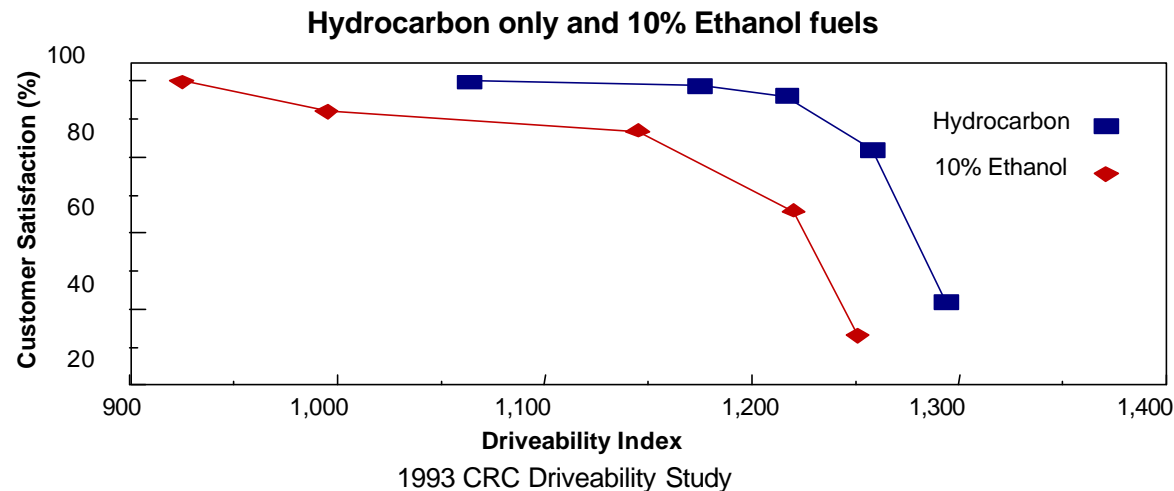
## Fuel System Requirements for EtOH-Containing Fuels

- At any temperature where the fuel Vapor Pressure is greater than the system operating pressure, vapor will form.
- Thermodynamics predicts when vapor will form, but not how much or where.
- Coordinating Research Council Work suggests that fuels should be limited to a vapor pressure of no more than 450 kPa at 250 degrees F.

# Vapor Pressure vs. Temp. for EtOH-Containing, and non-EtOH-containing Fuels

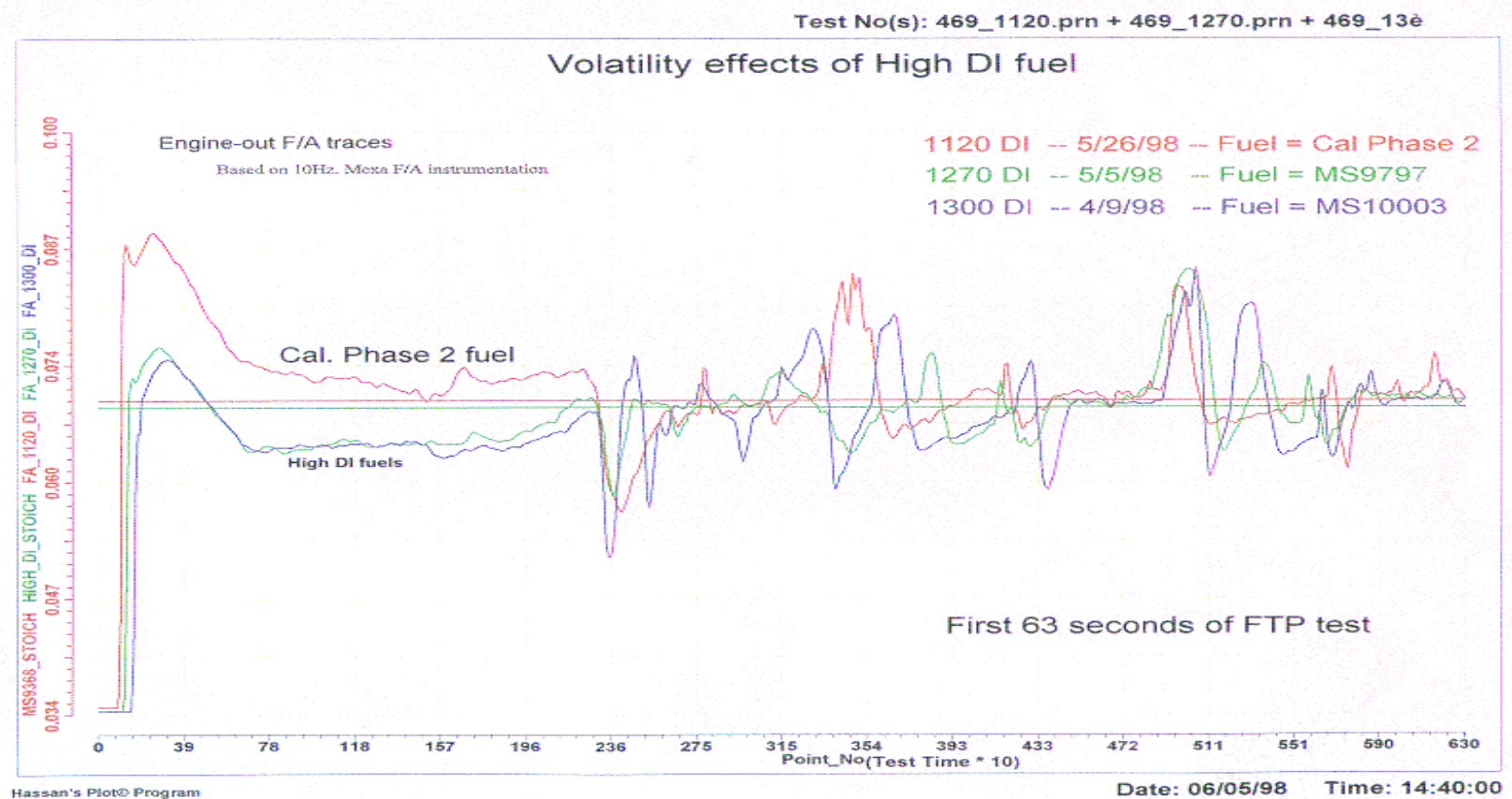


# Volatility Control Very Important to Vehicle Owners and Air Quality

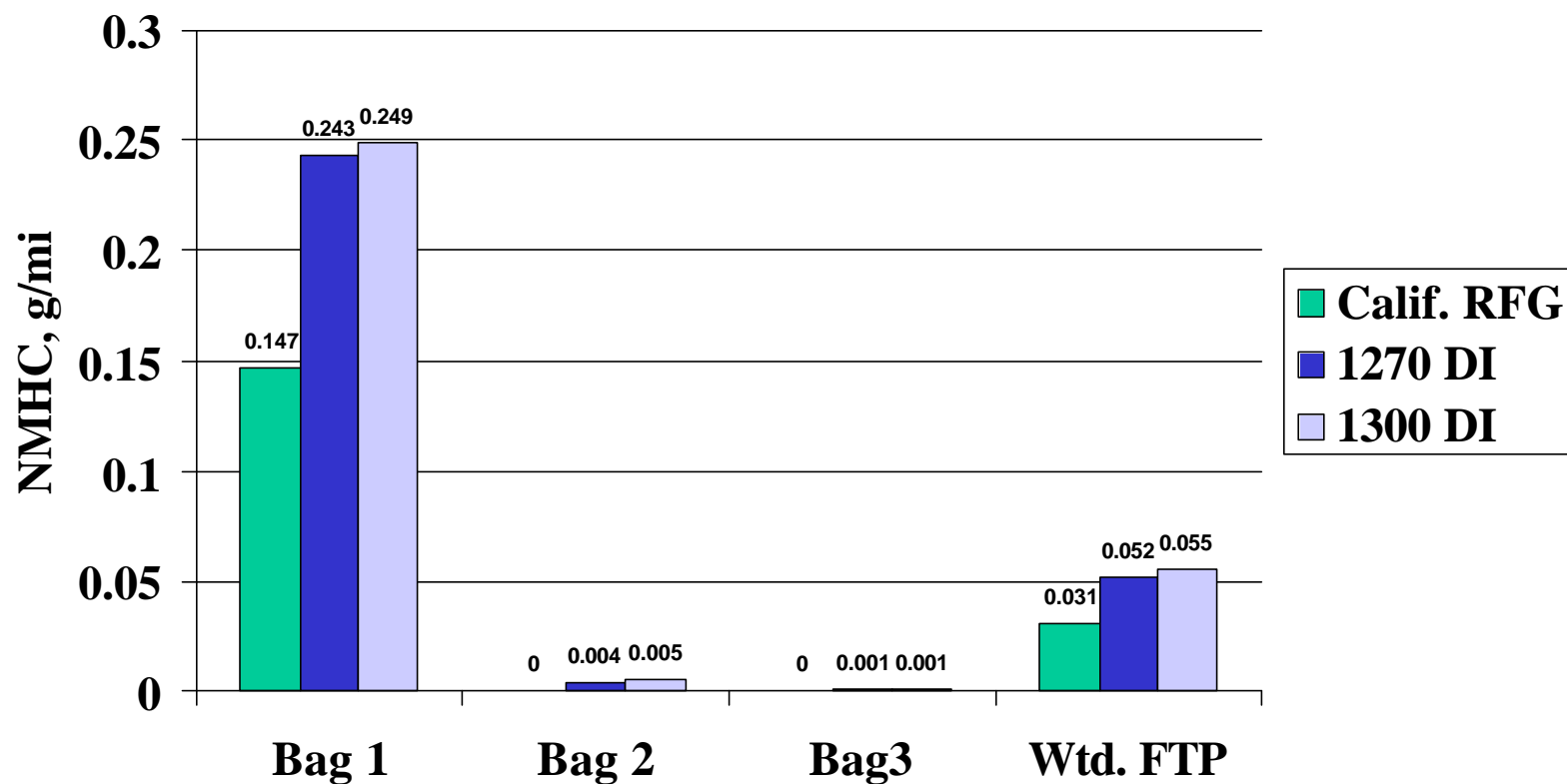


- Distillation Index =  $1.5 \cdot T_{10} + 3 \cdot T_{50} + T_{90} + 20 \cdot \text{wt oxygen from ethanol}$
- Equation based on CRC studies derived from consensus auto and oil industry research
- Worldwide Fuel Charter recommends 1200 maximum - endorsed by over 60 companies

# DI Effects on F/A Ratio Emissions from a 1998 ULEV



# DI Effects on NMHC Emissions from a 1998 ULEV





# Plusses and Minuses of Ethanol and C-8 Alkylate vs. MtBE

	Ethanol	C-8 alkylate
<b>Sulfur, Aromatics, Olefins</b>	<b>0</b>	<b>0</b>
<b>Octane</b>	<b>0</b>	<b>0</b>
<b>Minimum T50, Hot fuel handling</b>	<b>-</b>	<b>+</b>
<b>DI</b>	<b>0</b>	<b>-</b>
<b>Evap. Emissions</b>	<b>-</b>	<b>0</b>
<b>Permeation</b>	<b>-</b>	<b>+</b>

## Summary

- New vehicle standards must be accompanied by improvements in fuel quality, both to enhance the performance of existing technology for air quality improvements and to enable new technologies.
- Statewide, ARB has acknowledged the need for further emission reductions.
- Gasoline volatility plays a major role in vehicle performance and emissions
- Alkylates, although sulfur-, aromatic-, and olefin-free, C-8 alkylate as a replacement for MtBE will raise  $T_{50}$ , and the distillation index, thereby increasing emissions, and reducing vehicle performance, unless, some other heavy component is removed (heavy reformat?).
- Ethanol, reduces  $T_{50}$ , but not DI, and its impact on RVP will lead to higher evaporative emissions. Permeation needs to be studied further, but available data suggest a need for concern. Hot fuel handling can be managed, but only if the proper parameters are controlled.